

Total oxidation of lean propane over α -Fe₂O₃ using microwaves as an energy source

J. Dobosz · M. Zawadzki

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Abstract A combined process of catalytic oxidation and microwave heating for the treatment of lean propane-air mixture, and “green” hematite synthesis were described in this work. The study demonstrated that removal and oxidation efficiencies of propane over α -Fe₂O₃ were above 99.9 % after a short microwave radiation time (from 9 min) and they were strongly dependent on the applied microwave power. Comparing to conventional heating, the catalytic performance of hematite was enhanced by lowering the operation temperature under microwave conditions. Nanocrystalline α -Fe₂O₃ catalyst with mesoporous structure was successfully prepared by a microwave-assisted hydrothermal treatment of iron hydroxide in an aqueous solution without any alkali additive, and characterized by XRD, TEM, TPR-H₂, FTIR and N₂ adsorption–desorption. The microwave-induced heating over hematite catalyst appears to be a very effective alternative method for air treatment to the destruction and removal of short chain hydrocarbons.

Keywords Hydrothermal synthesis · Microwave heating · α -Fe₂O₃ · Propane combustion

Introduction

Nowadays, a lot of attention is paid to the processes for environmental protection. To control air pollution, catalytic deep oxidation is usually applied to decompose volatile organic compounds (VOCs) to final products such as CO₂ and H₂O [1]. However, conventional electric furnace heating, which is usually applied, faces many technical challenges in catalytic combustion, e.g. it is difficult to discharge

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reaction heat in time what may cause sintering and agglomeration of active phase leading to catalyst deactivation. Other drawbacks of electric furnace heating result from slow temperature adjustment of reaction bed and high energy consumption. Therefore, there is a significant need for a new heating method for catalytic total oxidation of VOCs.

In recent decades, growing interest in microwave heating for heterogeneous gas phase reaction systems has been observed [2–4]. Compared with conventional heating techniques, microwave heating offers not only higher heating rate and material selective heating, but also enhanced chemical reactivity and overall cost effectiveness. Microwave heating can significantly shorten the time of catalyst bed temperature adjustment. Moreover, because the temperature in the microwave chamber is much lower than in the catalytic bed, the reaction heat can be quickly released, which helps to keep the temperature of catalyst bed steady and to avoid problems connected with catalyst sintering. For these reasons, the application of microwave heating instead of conventional electric heating in catalytic oxidation processes seems to be a good choice.

Propane oxidation has been widely used as a model reaction to study the oxidation of short chain VOCs. A number of transition metal oxides and mixed metal systems containing Co, Mn or Fe ions have been shown promising activity for propane deep oxidation [5, 6] but only some of them were studied using microwaves as energy source. Will et al. [7] investigated LaCoO_3 , LaMnO_3 and $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$ catalysts and found small differences in propane conversion and CO_2 selectivity between experiments under microwave and classical conditions. Contrary to them, Beckers et al. [8] showed that propane oxidation was greatly enhanced by microwave irradiation over catalysts with perovskite structure.

Up to now, iron oxides were investigated in propane combustion only under classical heating and were found to show promising propane conversion to CO_2 for rich-in-oxygen mixtures [9, 10]. From the other side, it was shown that microwave energy can be very effective in the heating of iron oxides [11]. In spite of it, there are scarce literature data demonstrating that microwaves and iron oxides can be useful for the treatment of VOCs. The application of the microwave/ Fe_3O_4 catalytic system for the decomposition of acetone, n-hexane and dichloromethane was reported by Lee et al. [12] while the decomposition of isopropyl alcohol was recently studied by Chang et al. [13].

In the present work the microwave-assisted $\alpha\text{-Fe}_2\text{O}_3$ fixed-bed system was developed and used, for the first time, to investigate its ability for lean propane deep oxidation. Hematite was chosen as a catalyst because among iron oxides, it is the most stable under ambient conditions and the most environmentally friendly [14]. The catalyst was prepared by a “green” hydrothermal approach using microwave heating and amorphous iron hydroxide, treated in the neutral solution without any alkali or organic additives, as a single precursor. The physico-chemical properties of such obtained $\alpha\text{-Fe}_2\text{O}_3$ were characterized by several complementary methods like XRD, TEM, H_2 -TPR, FTIR and N_2 adsorption–desorption measurements. The effect of process parameters including microwave power and heating time, and propane concentration in the inlet gas were examined during propane catalytic

combustion. Moreover, microwave heating was compared to conventional heating under the same reaction conditions.

Experimental

Catalyst preparation

Iron(III) nitrate nonahydrate (reagent grade), ammonia (reagent grade) and distilled water were used as starting materials without further purification. First, iron(III) hydroxide was precipitated by the reaction of 0.25 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with 5 M NH_3 under vigorously stirring at room temperature for 1 h, next filtered off and repeatedly washed by distilled water to remove nitrate ions and ammonia excess. After that, a suitable amount of distilled water was added to the residue to obtain slurry of the concentration ~ 5 wt%. Such prepared aqueous reaction medium was put in a Teflon vessel and placed in an autoclave with microwave heating (ERTEC, Poland). Reaction was provided for 30 min at 140 °C under the autogenic pressure of ~ 10 bar. The obtained product was water washed and condensed following evaporation at elevated temperature. The resulting gel thus prepared was forced out in a wire from 3 to 4 mm in diameter by extrusion, air-dried at 180 °C overnight to remove any moisture, then crushed and sieved into the 0.6–1.2 mm particles.

Characterization methods

Phase identification of obtained materials was carried out using Powder X-Ray Diffraction (XRD). XRD measurements were performed in the 10–80 2θ range with a step of 0.026 and a time per step of 1 s using X'Pert Pro Panalytical diffractometer with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$). XRD data and the Scherrer equation were used to average grain size calculation.

The sample morphology and microstructure were analyzed by transmission electron microscopy (TEM/HRTEM). TEM images and SAED (Selected Area Electron Diffraction) patterns were recorded on Philips CM 20 SuperTwin microscope.

The textural characterization of the samples was achieved using conventional N_2 adsorption–desorption method at liquid nitrogen temperature, with an Autosorb-1 Quantachrome Instruments analyzer. The adsorption data were interpreted by the application of the Brunauer–Emmet–Teller (BET) method for the determination the specific surface area S_{BET} . The Barret–Joyner–Halenda (BJH) method was employed for pore size distribution calculations.

Temperature-programmed reduction (TPR- H_2) experiments were carried out in a Micrometrics Pulse Chemisorb 2705 instrument, equipped with a thermal conductivity detector (TCD). In the TPR measurements, 5 vol% H_2 in Ar at a constant flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ was used as a reducing gas, and sample was heated from the room temperature to 880 °C at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$.

Infrared measurements were carried out to confirm the samples purity. FTIR spectra were recorded by the BRUKERIFS-88 spectrometer in the region of

4,000–400 cm^{-1} with a spectral resolution of 2 cm^{-1} . The samples were prepared as *Nujol* mulls.

The catalytic activity measurements

The catalytic reaction was carried out under atmospheric pressure in a laboratory-scale continuous-flow reaction system with a fixed-bed quartz reactor of dimensions 12 mm I.O. \times 15 mm O.D. \times 450 mm L which could be placed in either a modified microwave oven (Westinghouse, with digital power level control and frequency of 2,450 MHz, modified as a continuously variable power setting mode) or in a conventional tubular furnace, by passing a gaseous mixture of propane and synthetic air over 1 g of the hematite catalyst placed on a quartz wool in the middle of the reactor. A schematic diagram of the experimental set-up used for the investigation of heterogeneous catalytic gas phase oxidation of propane under microwave heating conditions is shown in Fig. 1. A gaseous mixture propane/air, with volumetric gas composition of 2,000 or 1,000 ppmv C_3H_8 in air, was fed at a gas hourly space velocity (GHSV) of 4,800 h^{-1} for all the experiments, and gas flow was adjusted by mass flow controllers. The temperature measurements of the catalyst bed was performed in situ by an optical method (PhotoriX system, Luxtron) using sapphire rod for the light guide. The temperature was calibrated by comparing with thermocouple measurements (shielded, 3,7 mm diameter, ungrounded type K). Thermocouple was used to regular temperature measurements when conventional heating was applied or microwave power was switched off.

Microwave radiation was activated and uniformly followed for 30 min. The power was turned off automatically upon termination of the experiment, followed by natural cooling to room temperature and experiments were repeated in triplicate under the same conditions. Gas samples were collected in a Tedlar bags (SKC Inc., USA) periodically during microwave treatment at outlet of the reactor for the expected qualitative and/or quantitative analysis. Gas samples were analyzed by a gas chromatography (GC, PerkinElmer ARNEL, Clarus 500) equipped with a flame ionization detector (FID) for the determination of C_3H_8 analysis and TCD detector for CO and CO_2 analysis. A gas sampling loop and switching valve were used to inject gas samples to the GC from a by-pass line. Catalytic activity was evaluated determining both removing and oxidation efficiently of the catalyst as a function of the microwave radiation time. For comparison purposes, the catalytic performance of hematite using conventional electric heating was also examined. The conversion of propane as a function of the reaction temperature (*light-off curves*) was taken as a measure of catalytic activity. The activity was measured using triplicate gas chromatograph on-line injections during a 20 min hold period, and the catalyst was heated up to 500 $^\circ\text{C}$ (or, under microwave conditions, to the maximum obtainable temperature with the given microwave power) in 50 $^\circ\text{C}$ steps with a heating ramp of 5 $^\circ\text{C min}^{-1}$ (activity was measured at each temperature during the 20 min hold period). The relative standard deviation of three GC injections was generally below 3 %.

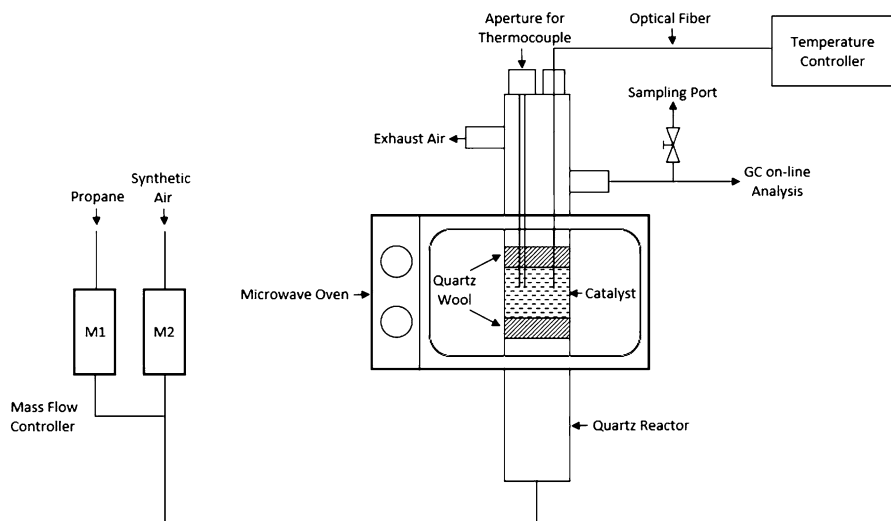


Fig. 1 Schematic diagram of the experimental set-up used for the investigation of heterogeneous catalytic gas phase oxidation of propane under microwave heating conditions

Results and discussion

Characterization of the catalyst

The purity and crystallinity of the as-prepared samples were examined by XRD technique. It could be concluded from Fig. 2a that precursor for hydrothermal treatment is amorphous Fe(III) hydroxide (JCPDS file Card, No. 22-0346). Fig. 2b displays the typical XRD pattern of the product obtained at 140 °C for 30 min. All the peaks can be well indexed to a pure rhombohedral structure (space group $R\bar{3}c$) of α -Fe₂O₃ (JCPDS file Card, No. 33-0664). No other peaks for impurities were observed. The diffraction peaks are not very strong or sharp, which indicates the nanocrystalline nature of the obtained iron oxide. The average crystalline size was 15 nm as calculated from the Scherrer equation. According to the literature data [15], it can be speculated that during reacting in hydrothermal environment, Fe(OH)₃ precursor is firstly transformed into hydrated iron oxide (α -FeOOH) phase through heat decomposition and then the obtained α -FeOOH is dissolved and converted into α -Fe₂O₃.

The morphological and structural information's of the as-prepared α -Fe₂O₃ nanoparticles were obtained from TEM investigations. The iron oxide aggregates with irregular shape and size of tens nm were obtained under microwave-assisted hydrothermal conditions. It could be observed from the TEM image (Fig. 3a) that all aggregates are composed of small particles in the range of 10–20 nm. The SAED pattern, shown as the inset in Fig. 3a, confirms the polycrystalline structure of α -Fe₂O₃ aggregates. This agrees well with the calculated crystal size from XRD data. HRTEM image in Fig. 3b presents the lattice fringes of individual nanoparticle. The

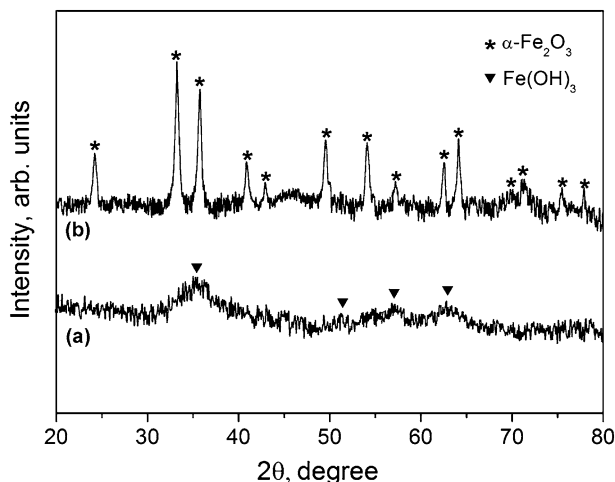


Fig. 2 XRD patterns of the precursor (a) and product (b) of hydrothermal synthesis at 140 °C for 30 min

inter-fringe distances were measured to be 0.17 nm, which corresponds well to the lattice spacing of the (116) plane of the rhombohedral hematite structure.

The texture characteristics of α - Fe_2O_3 samples were determined based on the nitrogen adsorption–desorption isotherms shown in Fig. 4. It should be noticed that hydrothermally prepared hematite displayed type IV nitrogen adsorption–desorption isotherms (according to IUPAC classification) with a hysteresis loop of type H1, characteristic of materials with interparticle mesoporosity. The pore size distribution curve presented as an *inset* in Fig. 4 shows that the as-prepared sample exhibits quite narrow pore size distribution with a maximum at ~ 13 nm. The calculated values of the specific surface area S_{BET} and total pore volume V_{total} amount to 38 m^2/g and 0.12 cm^3/g , respectively.

The reduction behavior of α - Fe_2O_3 examined by TPR- H_2 is shown in Fig. 5. The TPR- H_2 profile of α - Fe_2O_3 consists of two not well separated reduction peaks, the smaller low temperature peak (with maximum at about 440 °C) reflects the first stage of the reduction of hematite to magnetite ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$) and the second, broad and much larger, high temperature peak represents the reduction of magnetite to metallic iron. In fact, in this high temperature region, two heavily overlapped peaks could be observed suggesting the two-step magnetite reduction sequence $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. H_2 consumption corresponding to this high temperature reduction stage was 18.1 $\text{mmol H}_2/\text{g}_{\text{catal}}$, while the one corresponding to the low temperature step (reduction of hematite to magnetite) was 2.05 $\text{mmol H}_2/\text{g}_{\text{catal}}$. Generally, such reduction behavior of hydrothermally obtained nanocrystalline iron oxide with hematite structure is in line with the literature data [16].

Fourier transform infrared (FTIR) studies were performed to ascertain the metal–oxygen bonding and to confirm the purity of α - Fe_2O_3 prepared under microwave-assisted hydrothermal conditions. The FTIR spectrum of the as-prepared iron oxide powder is shown in Fig. 6. The observed vibration bands at low frequencies region

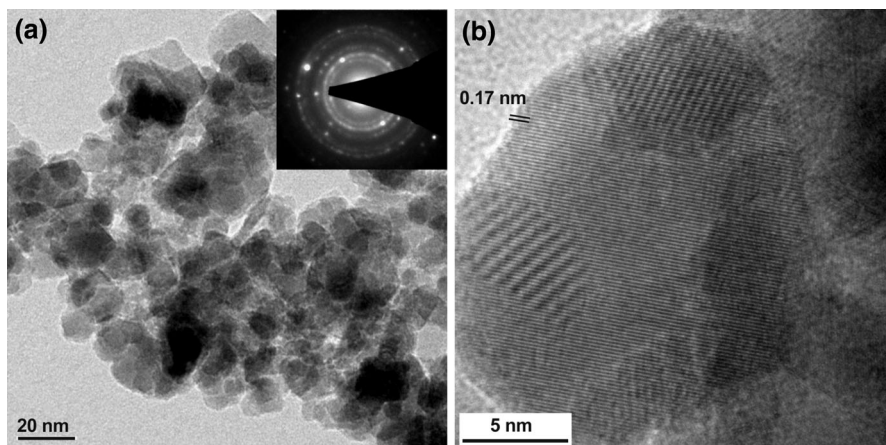


Fig. 3 Representative TEM (a) and HRTEM (b) images of hydrothermally prepared α -Fe₂O₃ with SAED pattern shown as *inset*

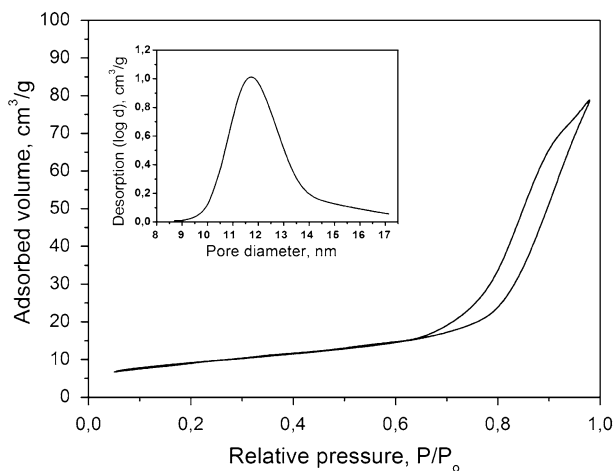


Fig. 4 N₂ adsorption–desorption isotherms of α -Fe₂O₃ with corresponding pore size distribution (as *inset*)

(at 463 and 562 cm⁻¹) may be assigned to Fe–O–Fe stretching vibration suggesting the formation of Fe₂O₃ with the hematite structure [17]. The FTIR spectrum displays also several bands associated with C–C and C–H vibrations which can be attributed to *Nujol*. From the infrared data, there is evidence that obtained α -Fe₂O₃ oxide is high purity and nanoparticles are not contaminated by foreign materials.

Therefore, the microwave-assisted hydrothermal method using only amorphous iron hydroxide as a precursor without any organic additives is very useful for the preparation of pure nanocrystalline α -Fe₂O₃ with improved textural properties. Literature data indicate that using conventional heating for hydrothermal treatment,

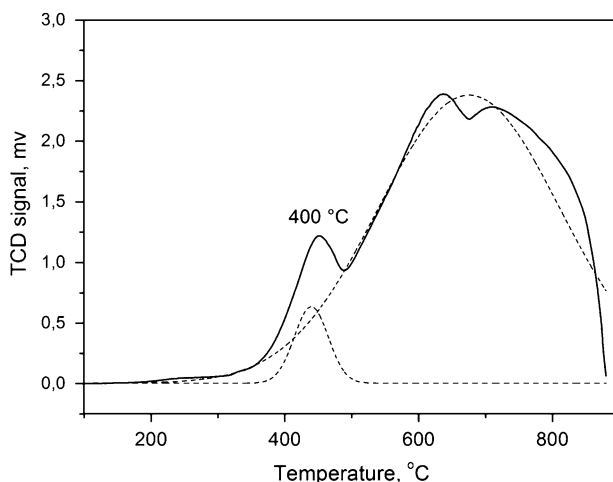


Fig. 5 TPR-H₂ pattern of α -Fe₂O₃ with deconvoluted profiles

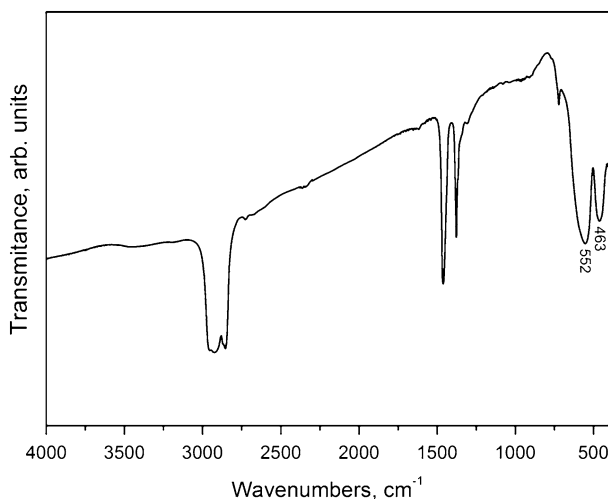


Fig. 6 FTIR spectrum of nanocrystalline α -Fe₂O₃

higher temperature and longer reaction time [18] or the presence of Fe(II) ions as catalyst [19] are needed to prepare nano-sized hematite particles but even so usually larger particles are obtained. The synthesis method applied in this work is particularly suited for the preparation of catalytic materials because smaller particle size and higher surface area are thought to lead to better performance in various reactions, among others, in the total oxidation of VOCs by metal oxide catalysts. Moreover, the particle size plays an important role in microwave heating. As reported by Ruan [20], dielectric loss of nanometer-sized particles is larger than that

of micrometer-sized particles, and nanocrystalline materials are usually better microwave absorbers.

Catalytic properties

Combustion of propane (C₃) in the inlet stream was carried out at steady state conditions using α-Fe₂O₃ fixed bed and microwave (MW) radiation process. The total C₃ concentration in inlet air stream was prepared equivalent to 2,000 or 1,000 ppmv and was adjusted at a gas hourly space velocity (GHSV) of 4,800 h⁻¹ for all the experiments.

Catalytic properties of α-Fe₂O₃ under microwave heating were evaluated taking into account both removal and oxidation processes and two efficiency types were determined, i.e. removal efficiency E_r (the efficiency of converting C₃ into any product) and oxidation efficiency E_{ox} (the efficiency of the C₃ conversion into carbon oxides):

$$E_r = \frac{(\text{VOC})_0 - (\text{VOC})_1}{(\text{VOC})_0} \times 100(\%)$$

Here (VOC)₀ is the initial concentration of C₃ and (VOC)₁ is the concentration of C₃ after microwave (MW) treatment,

$$E_{ox} = \frac{(\text{VOC})_{ox}}{(\text{VOC})_0} \times 100(\%)$$

Here (VOC)_{ox} is the amount of C₃ completely oxidized, as determined from the concentrations of CO and CO₂ after MW treatment.

First, the effect of different microwave power (in the range 100–750 W) on the temperature of the α-Fe₂O₃ fixed-bed was investigated under the absence of inlet gas and each run was held for 30 min. It was found that nanocrystalline α-Fe₂O₃ oxide is efficient absorbent of microwaves, since it absorbed microwave energy quite quickly and convert them into thermal energy within a short time, thus leading to the rapid increase of the catalytic bed temperature. It can be seen from Table 1 that the higher the MW power output is, the higher the rate of increase in temperature is and the higher temperature of the catalyst bed could be reach. It was observed that regardless of MW power, the temperature of the catalyst bed always reaches steady state of the thermal balance. Moreover, upon reaching the thermal balance temperature, an increase in the duration of MW radiation does not lead to further increase in the final temperature.

Blank tests, where propane was treated in the absence of α-Fe₂O₃, were performed to study if the destruction of this VOC was due to the MW radiation heat treatment. It was revealed that propane alone was not good absorbent for microwaves and its conversion not occurred at a MW power level up to 750 W.

Fig. 7 shows the removal efficiency E_r of propane as a function of MW radiation time at different MW power level. As can be seen, E_r reached value >99 % after 9 min of radiation with the power of 600 W. Applying the lower MW power level,

Table 1 Effect of microwave power on heating of hematite fixed-bed

MW power (W)	Heating rate (°C/min)	Final temperature (°C)
100	4.8	180
200	7.6	240
300	13.2	350
400	19.0	440
500	27.7	520
600	40.7	590
750	55.8	690

prolonged radiation time is needed to reach an efficiency close to 100 %, i.e. 12, 18 and 26 min at 500, 400, and 300 W. This reveals that nanocrystalline α -Fe₂O₃ does not play only a role of the thermal medium (possessing much greater microwave capacity than propane) during combustion of propane under MW radiation but also works as an active catalyst. The effect of propane concentration is also shown in Fig. 7, at power level of 300 W, indicating that both for 2,000 and 1,000 ppmv the E_r is very similar. It indicates that nanocrystalline α -Fe₂O₃ oxide is very efficient in destroying and removing of propane under MW treatment, regardless of its concentration, and appropriately the low microwave power can be used.

The usefulness of α -Fe₂O₃ for microwave-induced propane combustion in excess of oxygen was confirmed by appointing its oxidation efficiency E_{ox} . It was stated that CO₂ was the only oxidation product, the concentration of CO was close to the background and undetected by the instrument. Fig. 8 shows the E_{ox} plot versus microwave radiation time for propane of 2,000 ppmv in the rear gas treated with MW power of 600 W in the presence of α -Fe₂O₃ catalyst. The propane oxidation efficiency increases as a function of MW radiation time up to near 100 % after about 9 min. indicating that propane in the inlet stream was completely decomposed into the final products CO₂ and H₂O. The calculated mass balance of C between input propane and output CO₂ during the microwave-induced process evidenced the same result, i.e. above 99.9 %. The effect of MW power level and propane concentration on oxidation efficiency E_{ox} (not shown) was very similar to that for removal efficiency E_r , i.e. maximum value of CO₂ concentration, regardless of propane concentration, was observed from about 12 to 26 min for MW power from the range 500–300 W. Moreover, it could be noticed from Fig. 8 that deviations of the propane conversion level are very insignificant as the microwave radiation process was lasting longer than time essential to achieve conversion above 99 %. For a prolonged time, the concentration of propane in the outlet stream was found to be close to the detection limited level by a GC analysis. It suggests that total destruction of propane over nanocrystalline α -Fe₂O₃ fixed-bed catalyst can be achieved for continuous (long time) microwave-induced radiation process.

The long-term stability tests (oxidation efficiency in terms of the time-on-stream) have been investigated and the results are shown in Fig. 9 for the two MW power

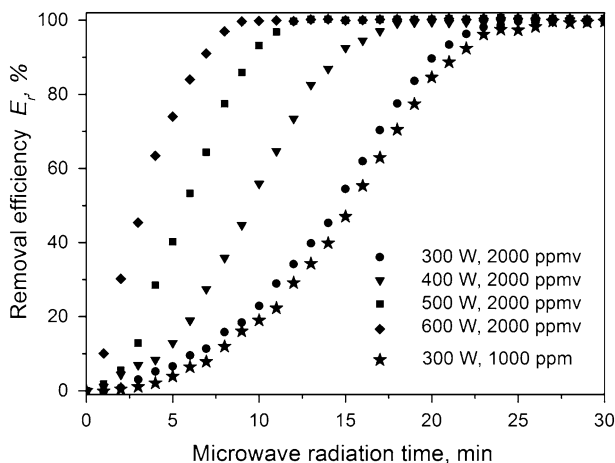


Fig. 7 Removal efficiency profiles (E_r) of propane over microwave radiated $\alpha\text{-Fe}_2\text{O}_3$ at different MW power levels, for propane concentration in the inlet stream equal to 2,000 and 1,000 ppmv

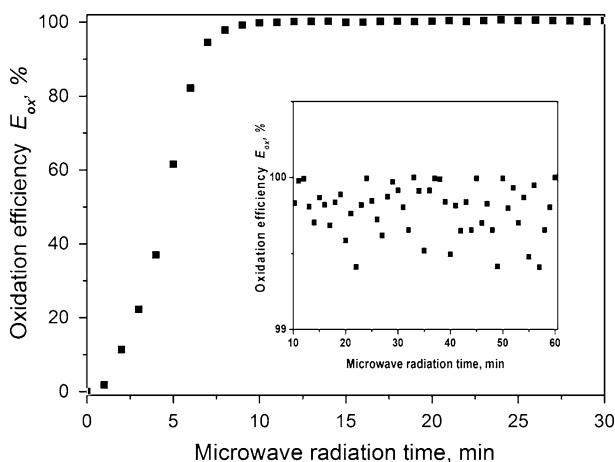


Fig. 8 Oxidation efficiency profile (E_{ox}) of propane over microwave radiated $\alpha\text{-Fe}_2\text{O}_3$ at MW power levels of 600 W, for propane concentration in the inlet stream equal to 2,000 ppmv. The effect of prolonged MW radiation time on E_{ox} is shown as *inset*

applied, 300 and 600 W. It should be noticed that no significant catalyst deactivation takes place on stream both at high and low conversion level what confirms good catalyst durability and suggests that microwave heating, regardless of MW power used, does not damage the catalyst, at least for the reaction conditions and the reaction time chosen. Good catalyst stability is in line with the observations that physicochemical characteristics of the catalyst did not change after the catalytic test (XRD of the used catalyst—not shown—demonstrated the same crystal structure and very similar average crystallite size as for the fresh catalyst).

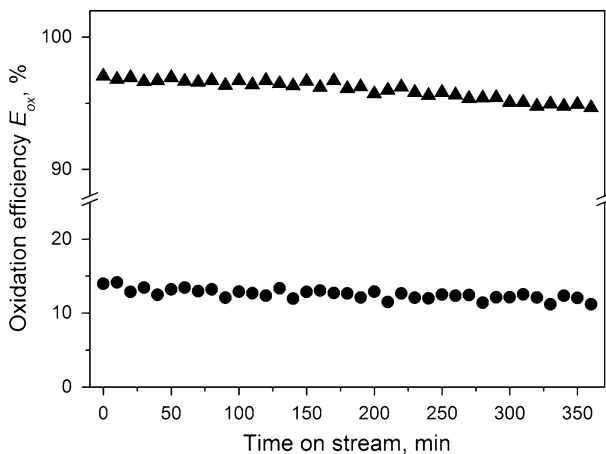


Fig. 9 Time-on-stream test for α -Fe₂O₃ catalyst at low and high propane conversion level at MW power level of 300 and 600 W, respectively

The catalytic behavior of hematite confirms results reported in the literature results for other catalysts, which indicated that oxidation reactions of VOCs under microwave conditions can proceed quickly and efficiently. Chang et al. [13] showed high removal efficiency of isopropyl alcohol over magnetite ($\geq 99\%$ in 15 min, for MW power at a level of 750 W) while Lee et al. [12] revealed that Fe₃O₄ is very efficient in destroying an removing of acetone, dichloromethane and *n*-hexane which could be decomposed completely at a power level of 645 W at heating time of 10 min. The results of Bo research [21] showed that catalytic oxidation of toluene waste gas by CuO/zeolite catalyst mixed with microwave-absorbing material (SiC) was feasible with removal rate higher than 90 %.

We also compared the catalytic activity of nanocrystalline α -Fe₂O₃ under conditions of microwave and conventional heating assessing the propane conversion against the catalyst bed temperature. The obtained *light-off* curves are shown in Fig. 10 and indicate that with microwaves, irrespective of the MW power used (600, 500 or 300 W), the same amount of propane conversion is reached in much lower temperatures in the comparison to conventional heating: both $T_{50\%}$ (temperature corresponding to 50 % conversion) and the total conversion was observed up to 100 °C lower. It indicates that under microwave conditions, the reaction temperature at some sites in the catalyst bed was higher than the average temperature measured suggesting the presence of so-called “hot spots”. Reactant molecules adsorbed on such a hot active sites may be activated by a subsequent energy transfer from the site to the adsorbed molecule. Therefore, the generation of “hot spots” is of great importance because reactions on active sites may take place at much higher temperatures than at the measured bulk temperature of the catalyst. As a result, the catalytic activity is higher than under conventional heating. If such phenomena occur it could be concluded, comparing the *light-off* curves received at different microwave powers, that for higher MW power the temperature of created “hot

spots” is higher and/or their amount is significantly larger. The microwave thermal effect is then higher and catalyst is more efficient in the total oxidation of propane (*light-off* curves are shifted to the lower temperatures).

It has been already postulated that dielectric heating may result in selective heating of catalytic sites with respect to their direct surroundings thus leading to the formation of higher temperature sites or points usually referred to as “hot spots” [22, 23]. These “hot spots” have temperatures 100–200 °C above that of the remainder of the bulk and are primarily considered to be the mechanisms responsible for the enhanced reaction rate. Hot spots may be also created by the difference in dielectric properties of materials or by the uneven distribution of electromagnetic field strength [24]. Unfortunately, the microscale nature of this phenomenon induces technical problems with direct measuring the temperature of “hot-spots” by the available techniques, and hence experimental proof of their existence is lacking. However, Matsubara et al. [25], studying surface temperature distribution based on the thermal radiation spectrum due to the microwave heating of iron oxides (magnetite and hematite), observed the creation of local hot domains in the order of tens μm which generated huge temperature gradient of $\sim 200\text{--}400$ °C. Zhang et al. [26] studying the catalytic decomposition of hydrogen sulfide under microwave heating postulated that observed catalyst structure reorganization, phase change from γ -alumina to α -alumina at unusually low measured temperature, could be the evidence for the formation of “hot spots”, although their exact location in the catalyst bed was difficult to determine. Generally, in every literature report, when enhancement of the catalyst oxidation behavior under microwave radiation conditions is observed, it is assigned to the “hot spot” formation, regardless of the physicochemical properties of the used catalyst. Among others, Zhang-Steenwinkel et al. [27] proposed that local “hot spots” on the surface of $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ catalyst can explain the increased activity during CH_4 oxidation, and Liu et al. [28] postulated that improved oxidation of *o*-xylene was due to the existence of “super-heated molecules” as active sites. But there are only few reports concerning propane total oxidation under microwave radiation using mixed oxides as catalysts. Beckers et al. [8, 29] revealed that most of studied doped perovskites give higher propane conversion rates and suggests the hypothesis that MW heating creates “hot spots” on the catalysts active sites depending on the nature of occupied B site atom in the perovskite structure and its number of unpaired d-electrons. The most active $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ enables full propane conversion at 350 °C i.e. about 200 °C lower than under conventional heating. Will et al. [7, 30], however, investigating the similar perovskite catalysts, found small differences in propane conversion and CO_2 selectivity between experiments under microwave and classical conditions. In both cases, the temperature of full propane conversion was >600 °C for $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ catalyst but, as compared to the Beckers report, it was prepared in a different way and was characterized by some different properties, among others, by slightly lower surface area. Krech et al. [31] comparing microwave and conventional propane oxidation showed that nanoscaled perovskite catalysts, for which the higher surface area could be expected, can exhibit different behavior than non-nanoscaled perovskites which should have lower surface area. The catalytic activity under microwave conditions was higher in the case of non-nanoscaled perovskites, which was explained with suggestion that the size of

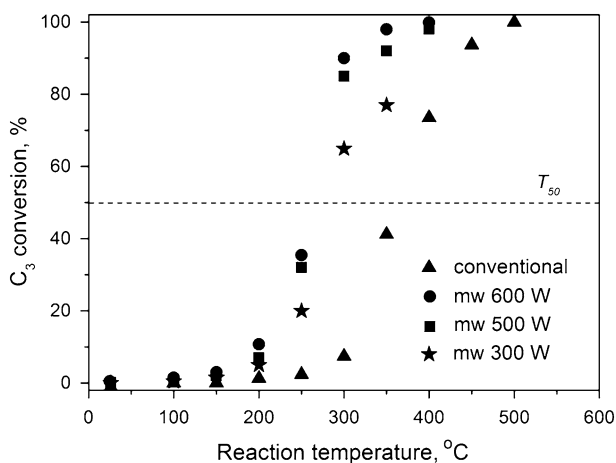


Fig. 10 Conversion of propane over α -Fe₂O₃ as a function of temperature for microwave heating at various MW power levels in comparison to conventional heating (2,000 ppmv C₃H₈ in air, GHSV = 4,800 h⁻¹)

nanoscaled perovskite particles was too small and microscopic “hot spots” could not appear. When the behavior of nanoscaled perovskites was compared in terms of these two heating methods, no significant difference was detected. The most active non-nanoscaled La_{0.8}Sr_{0.2}MnO₃ catalyst enabled full propane conversion at 400 °C while other studied perovskites at much higher temperatures. But the authors did not specify exactly the differences between them, in terms of particle size and surface area, so postulated relation between these properties of studied catalysts and their behavior under microwave heating is not clear. However, it seems that further, systematic investigations are needed to explain the catalytic oxidation behavior of mixed or single metal oxides under microwave heating, taking into account the effect of their textural properties (specific surface area and porosity) and particle morphology (shape and size), and particularly the relationship between these properties and formation of “hot spots”.

The experimental results of our study showed that the use of microwave energy enables not only the fast and efficient heating of α -Fe₂O₃ catalyst but also significantly enhances its combustion properties by lowering the operation temperature. Based on the literature data, it can be stated that catalytic activity for propane total oxidation of nanocrystalline hematite and the most active Sr doped LaMnO₃ catalysts are very similar under the microwave heating conditions. The method of microwave induced destruction of lean propane in the presence of α -Fe₂O₃ can be seen then as potential alternative to the conventional process and seems also to be an attractive and promising alternative for the removal of other, than light VOCs, air pollutants.

Our future work will be the optimization of catalytic microwave system and treatment of multi-component VOCs gases. Preparation of iron oxides catalysts with various textural properties and particle morphology as well as selection of other catalytic systems will also be considered too.

Conclusions

An experimental approach was adopted to explore and quantify the benefits coming from the microwave heating used for the total oxidation of lean propane, as representative light VOCs molecule, over α -Fe₂O₃ oxide in a continuous flow reaction system. It was found that removal and oxidation efficiencies of propane over α -Fe₂O₃ were above 99.9 % after short microwave radiation time and they were strongly depended on the applied microwave power. Moreover, the catalytic performance of hematite under microwave conditions was enhanced by lowering the operation temperature as compared to conventional heating. It was attributed to the formation of “hot spots” having higher temperatures than the average temperatures measured in the bulk catalyst. High purity nanocrystalline α -Fe₂O₃ catalyst with mesoporous structure has been successfully prepared by a microwave-assisted hydrothermal treatment of iron hydroxide in an aqueous solution without any alkali additive. Experimental results suggest that nanocrystalline α -Fe₂O₃ material may be useful for destruction of other short chain VOCs under microwave treatment.

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